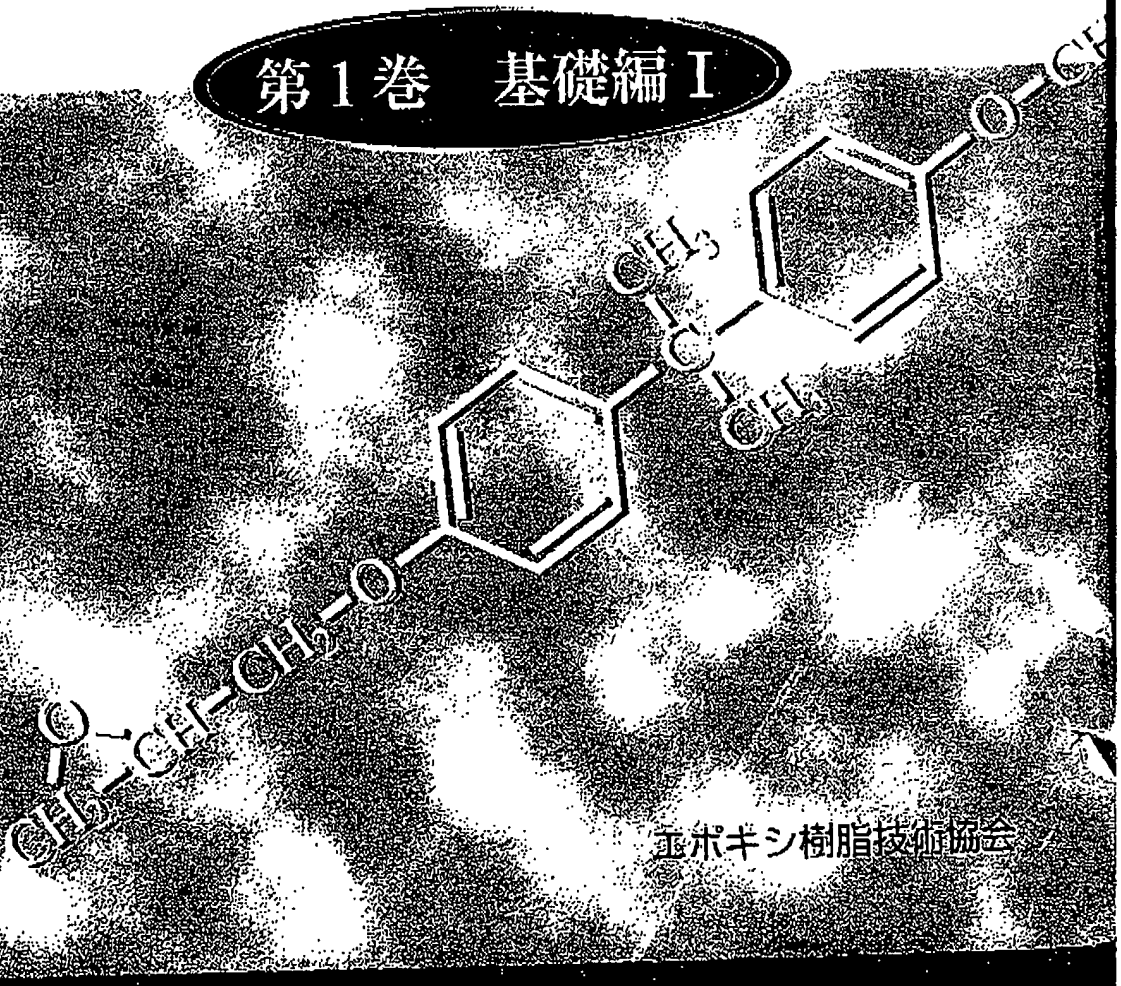
総説

エポキシ樹脂

Epoxy Resins

第1巻 基礎編 I



エポキシ樹脂技術協会

２００３年 １１月１９日刊行

総説 エポキシ樹脂

エポキシ樹脂技術協会編
編集委員長 垣内 弘（横浜国立大学名誉教授）

Ｂ５版／全４巻、全約１，１００頁、上製本（ケース入り）／定価３０，０００円（税込み）			
第１巻：基礎編Ⅰ	第２巻：基礎編Ⅱ	第３巻：応用編Ⅰ	第４巻：応用編Ⅱ
各巻、241～316頁 各巻毎の価格／定価７，５００円（税込み）			
編集・発行 エポキシ樹脂技術協会			

（刊行の趣旨）
商業化から６０余年を経てきたエポキシ樹脂は、その時代の先端技術を支える高機能材料原料として形を変えながら発展してきた。当協会の創立３０周年記念事業として、２１世紀のさらなる発展に期待し、産学の権威者を編集委員に迎え、各分野の第一線の研究・開発技術者に執筆を依頼し、エポキシ樹脂の基礎から応用技術までを集大成し出版するに至った。産業や教育の場で研究者、技術者の座右の書として活用され、エポキシ樹脂関連産業のさらなる発展に寄与することを期待したい。

購入受付中 （ネット特価販売）

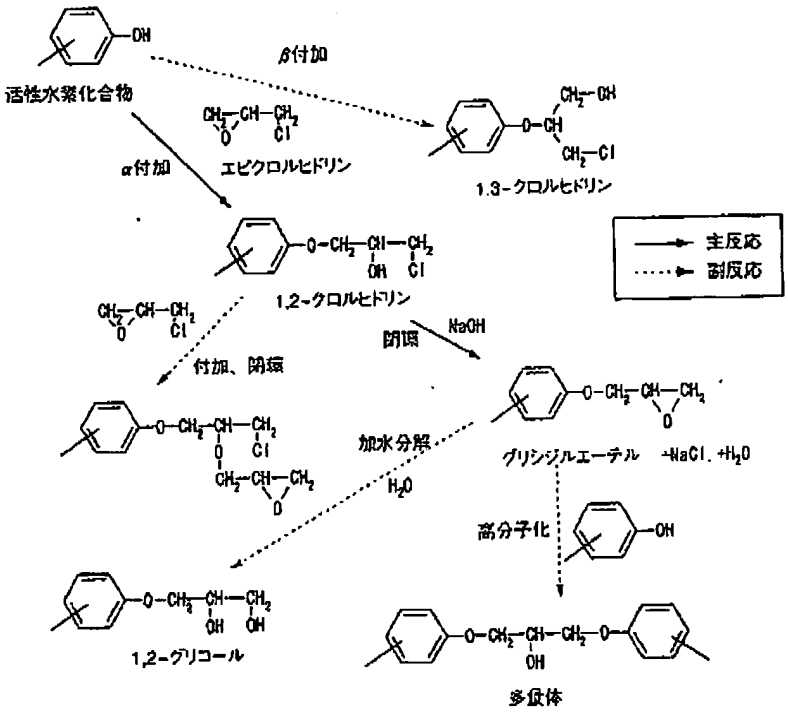


図3 エポキシ樹脂の製造反応

脂と同様に大過剰のエピクロルヒドリンを使用する。分子量の調整は，原料のノボラック樹脂の分子量で行われる。

(iv) 副反応

一般の化学反応と同ように上記の主反応に伴って種々の副反応が起こる。その主な物は，エピクロルヒドリンのβ付加による1,3-クロルヒドリン体の生成，1,2-クロルヒドリン体の水酸基へのエピクロルヒドリンの付加による塩素系不純物の増加，水分の付加によるグリコール基の生成，主鎖中の2級水酸基へのエポキシ基の付加による分岐の発生などである。

実際のエポキシ樹脂の生産においては，目的の性状，性能の製品を効率よく得るために，各主反応の転化率の調整や各副反応のコントロールが精密に行われている。近年においては，電子分野で用いられるエポキシ樹脂の高純度化（低塩素化）が求められ，副反応の抑制や精製方法について精力的に研究された[3]。

b）二段法

上記のようにして得られた低分子量のエポキシ樹脂に，活性水素を2個以上持つ化合物（ビスフェノール類など）を反応させることにより，分子量を伸ばしたり，難燃性などの機能を付与する方法があり，二段法あるいはアドバンスド（またはアドバンス）法，フュージョン法などとよばれている。

固形エポキシ樹脂は，前記のエピクロルヒドリンから直接作る一段法とこの二段法のどちらでも製造できるが，その性状は若干異なってくる。最も大きな違いは分子量分布であり，一段法品は，各成体をバランス良く含んでいるが，二段法品は，主に奇数成体からなる。この結果，エポキシ当量と軟化点や粘度とのバランスがずれてくる。また，末端基組成なども異なってくることが多い。さらに，

Reference 1

Re: Bibliographical Description

Title: "Epoxy Resins"
Editor: "The Japan Society of Epoxy Resin Technology" (The members of Editorial Board: Hiroshi Kakiuchi et al.)
Publication Date: November 19, 2003

Partial English Translation in page 23 of Vol.1

Re: Figure 3 in Page 23

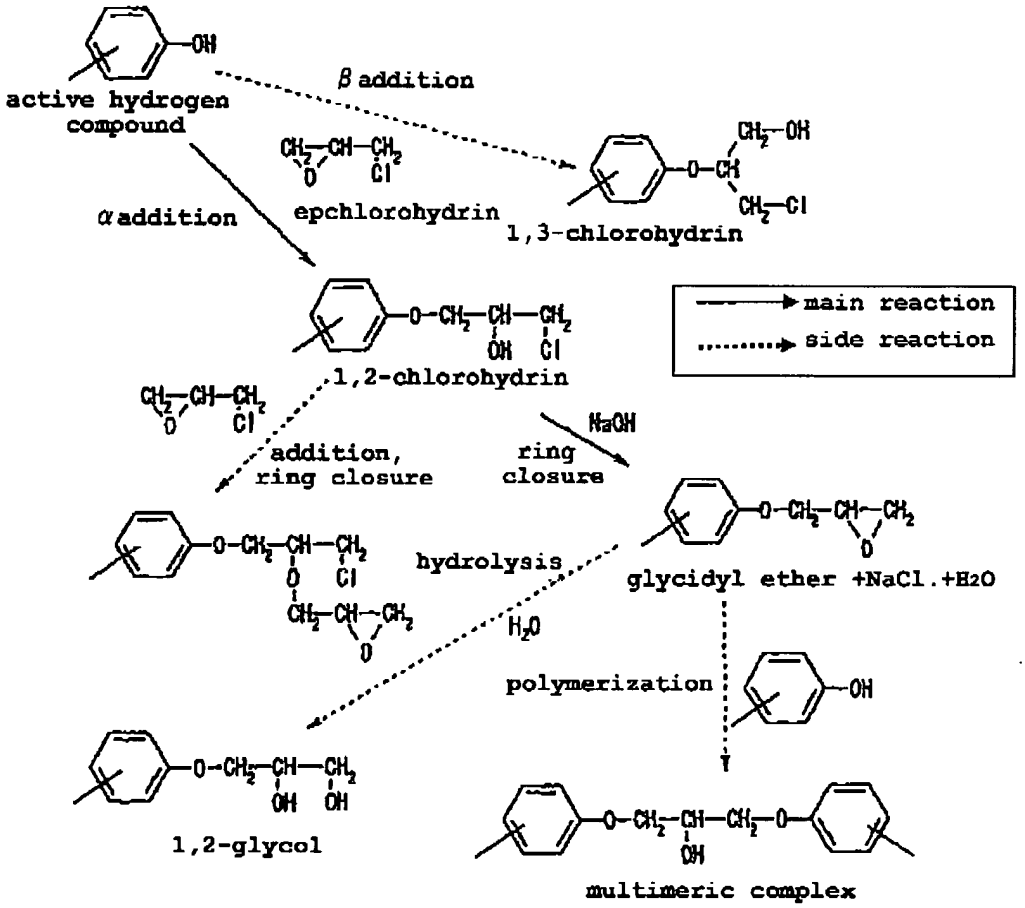


Fig. 3 Reactions in Preparing Epoxy Resin

Re: Item (iv) in Page 23

(iv) Side Reaction Products

As seen in many general chemical reactions, the various side reactions occur with the above main reaction. The main side reactions of them are the formation of 1, 3 - chlorohydrin by a β-addition of epchlorohydrin, the increases of the chlorine impurities by an addition of epchlorohydrin to hydroxyl group of 1, 2 - chlorohydrin, the formation of glycolic group by an addition of water, the occurrence of branches by an addition of epoxy group to a sec-hydroxyl group in the main chain, and so on.

When the epoxy resin is actually prepared, the adjustment of conversion efficiency in each reaction and the control of each side reaction are precisely conducted in order to efficiently produce the products with the desired properties and abilities. Recently, the high purity (the low chlorination) of epoxy resin is demanded in the electric fields, the method for the suppression of the side reactions and the method for the purification has been aggressively developed.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :

TAKETOSHI USUI ET AL. : GROUP ART UNIT: 1796

Serial No. 10/532,300 :

Filed: November 26, 2003 : EXAMINER: ARNBERG, MEGAN

For: CAPUSLE TYPE CURING AGENT :
AND COMPOSITION :

D E C L A R A T I O N

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

I, Yoshikimi KONDO, a Japanese citizen, c/o Asahi Kasei Chemicals Corporation, 1-2, Yuraku-cho 1-chome, Chiyoda-ku, Tokyo, Japan, declare:

That I am familiar with the invention of the above-identified application and the prosecution history of the application;

That I have read and understand the official action issued against the above-identified application on January 28, 2008 and the prior art references cited therein;

That in order to prove that the capsule curing

agent which comprises a core of the present invention is different from that of Ishimura et al., EP 0304503, I conducted the following experiments:

EXPERIMENTS

The following experiments were conducted in the laboratories of Fuji branch office at Asahi Kasei Chemicals Corporation on June 12 and 13, 2008.

[I] Measurement of Total Amount of Chlorines in Epoxy Resin "AER-331"

(i) Summary of Analytical Methods

Epoxy resin "AER-331" in a nonaqueous solution was dissolved under the conditions of an excess KOH solution at high temperature, and then the generated chlorine ions therein were titrated with an aqueous solution of silver nitrate.

(ii) Apparatuses and Instruments Used in Experiment

1: Potentiometric Titration Apparatus (AT-118 or AT-420 Platinum electrode manufactured by Kyoto Electrics Manufacturing Corporation Ltd.)

2: Hot Plate

3: 300 ml Beaker with Cover

4: Scale Balance

5: Stopwatch

6: 200 ml Measuring Cylinder

7: Liebig Condenser

(iii) Reagents

1: 1160 mol/m^3 (1.16 mol/l) of propylene glycol solution of KOH

2: 10 mol/m^3 (0.01 mol/l) of $AgNO_3$ aqueous solution

3: Butyl carbitol (Guaranteed Reagent)

4: Glacial Acetic Acid (Guaranteed Reagent)

(iv) Operations

1: Sample of epoxy resin "AER-331" in a 300 ml beaker with cover was weighted to be 1-5g with an accuracy of 0.0001 g.

2: About 25 ml of butyl carbitol was added thereto, and then the beaker was heated on a hot plate to dissolve the sample.

3: About 25 ml of the above propylene glycol solution of KOH was further added thereto, and then was sufficiently mixed.

4: The above condenser was attached to the beaker, and the beaker was placed on the hot plate. And then, the beaker was heated with stirring thereon. The hot plate was set at 300°C.

5: The heating was accurately conducted for 10 minutes after starting the drop of the condensate liquid from the above condenser.

6: After then, the hot plate was removed, and the beaker was cooled down to the room temperature using a water bath.

7: After cooling, 200ml of acetic acid was added.

8: The above condenser was removed after cooling, and

the beaker was set on the above potentiometric titration. And then, the above $AgNO_3$ aqueous solution was titrated in the beaker.

(v) Calculation

The total amount of chlorines (ppm) in the sample of epoxy resin "AER-331" was calculated using the following calculation formula.

Total amount of chlorines (ppm) = $\{(V-V_0)\times f\times 10\times 35.5\} / W$

W: Weight of Sample(g);

V: Titer(ml);

V_0: Blank Titer(ml);

f: $AgNO_3$ factor.

(vi) Results

The total amount of chlorines (ppm) in the sample of epoxy resin "AER-331" was 1500 ppm.

[II] Effects of Total Amount of Chlorines in Epoxy Resin on Storage Stability and Hardening Property of Epoxy Resin

Regarding two cases where the total amounts of chlorines in epoxy resin were 389 ppm and 1500 ppm, the effects of them on the storage stability and hardening property of the epoxy resin were examined.

Specifically, the effects of the case where the total amount of chlorines in the epoxy resin was 1500 ppm on the storage stability and hardening property of the

epoxy resin were examined in the same way as Example 8 of the present specification. This is because as shown in Table 2-2 of the present specification, Example 8 discloses the effects of the case where the total amount of chlorines in epoxy resin was 389 ppm on the storage stability and hardening property of the epoxy resin.

The results are summarized in Table 1.

Table 1: Effects of Total Amount of Chlorines in Epoxy Resin on Storage Stability and Hardening Property of Epoxy Resin

Manufacturing of core-shell type hardening agent		
Total Amount of Chlorines in Epoxy Resin	389 ppm	1500 ppm
Name of hardening agent	H-8	H-11
Amine compound	A-6 100 parts	A-6 100 parts
Epoxy resin	B-2 200 parts	E-2 200 parts
Water	1 part	1 part
Isocyanate compound	TDI*1 5 parts	TDI*1 5 parts
Shell forming	40 °C	40 °C

conditions	48 hours	48 hours
Shell intermediate layer composite / core (wt. ratio)	0.40	0.18
C-13 NMR Peak height ratio in C-13 NMR	10.1	2.8
IR measurement Bond (X) Bond (Y) Bond (Z)	 Observed Observed Observed	 Observed Observed Observed
Storage stability of epoxy resin composition	100 %	33 %
Curability of epoxy resin composition	130 °C	120 °C

*1: TDI (= Tolylenediisocyanate)

The effects of the case where the total amounts of chlorines in epoxy resin were 389 ppm was much better than those of the case where the total amount of chlorines in the epoxy resin was 1500 ppm in terms of both of the storage stability of epoxy resin composition and the curability of epoxy resin composition.

The undersigned declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this day of June, 2008.

19, June, 2008

Yoshikimi Kondo

Yoshikimi KONDO